

Effect of Protonation on Hole Superexchange
Across Gold / Osmium Bis-bipyridyl Tetrazine
Chloride Monolayer Interfaces

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Monolayers of $[\text{Os}(\text{bpy})_2 \text{ 4-tet Cl}]^+$, where bpy is 2,2'-bipyridyl and 4-tet is 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine, have been formed by spontaneous adsorption onto clean gold microelectrodes. These monolayers are extremely stable and exhibit well defined voltammetric responses for the $\text{Os}^{2+/3+}$ redox reaction across a wide range of solution pH values. The shift in the formal potential with increasing perchlorate concentration indicates that the oxidized form is ion-paired to a single additional perchlorate anion. The tetrazine bridge between the $[\text{Os}(\text{bpy})_2 \text{ Cl}]^+$ moiety and the electrode surface undergoes a reversible protonation/deprotonation reaction depending on the pH of the contacting electrolyte. The pK_a of the tetrazine within the monolayer has been determined as 2.7 ± 0.3 from the pH dependence of the interfacial capacitance. This value is indistinguishable from that found for the complex dissolved in essentially aqueous solution suggesting that these monolayers are highly solvated. High speed cyclic voltammetry reveals that the redox switching mechanism is best described as a non-adiabatic, through-bond tunneling process. Significantly, while protonating the bridging ligand does not influence the free energy of activation, $10.3 \pm 1.1 \text{ kJ mol}^{-1}$, k° decreases by an order of magnitude from 1.1×10^4 to $1.1 \times 10^3 \text{ s}^{-1}$ upon protonation of the bridge. These observations are interpreted in terms of a through-bond hole tunneling mechanism in which protonation decreases the electron density on the bridge and reduces the strength of the electronic coupling between the metal center and the electrode.